(apparent) is not very well determined. Its hydroxide ion dependence is, thus, relatively unknown. It is only considering our experimental errors that we suggest its independence of the hydroxide ion concentration.

In addition to the closely related octaammine system[17] discussed previously, a number of other systems have also been reported, particularly those dealing with chromium analogs.[18,19] In all of these systems, a singly hydroxo-bridged dimer is suggested as an intermediate in the hydrolysis. As far as we know, no base hydrolysis has been reported for these or similar complexes.

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Bridging and Nonbridging Ligand Effects in Some Reversible Reductions of Macrocyclic Complexes of Cobalt(III)[1]

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The reversible one-electron reductions of *trans*-$CoL(OH_2)_2^{3+}$ (L = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene or 5,7,7,12,14,14-hexamethyl-1,4,7,11-tetraazacyclotetradecane) by $Ru(NH_3)_6^{2+}$, Cr^{2+}, and V^{2+} have been examined. The outer-sphere $Ru(NH_3)_6^{2+}$ reductions are more rapid than similar reductions of $Co(NH_3)_5OH_2^{3+}$ and $Co(NH_3)_6^{3+}$ with differences in reactivity being very close to those predicted from variations in the oxidation potentials of the cobalt(II)–cobalt(III) couples. The variations with $[H^+]$ of reaction rate show the expected qualitative trends for $Ru(NH_3)_6^{2+}$ (rate decreases with increasing pH) and Cr^{2+} (rate increases with increasing pH). However, the acid dependence of the Cr^{2+} reactions is complex in its details and the total chemical behavior is not compatible with the "classical" attribution of an extraordinary electron mediating (or "conducting") capacity to an OH^- bridging ligand.

Despite the large number of mechanistic studies involving cobalt(III) oxidants,[4] explanations of the range and patterns of reactivity are in many cases controversial or still lacking. It has been particularly difficult to obtain experimental information which reflects on the role played by bridging ligands in inner-sphere electron-transfer reactions.[4] The experimental ambiguities contrast with the considerable interest in theoretical models of possible mediating effects of such bridging ligands.[5-9] Many of the key issues are dramatized by comparisons of the rates of reactions in which hydroxide functions as a bridging group to reactions which are bridged by a water molecule. In the mechanistically clear cases of Cr^{2+} reductions of cobalt(III) oxidants,[10-12] an enhancement of about 10^6 has generally been attributed to the hydroxy-bridged path over the aquo-bridged path. There has been a tendency to view this enhancement of rate as the result of some unique mediating property possessed by OH^- to a greater extent than by H_2O. This view has persisted[13] in the face of several considerations which should have raised serious doubts: (1) the hydroxy complexes should be thermodynamically more difficult to reduce (owing to the relative instability of the cobalt(II) hydroxide; this effect apparently dominates in the corresponding outer-sphere reactions[14,15]); (2) OH^- should have a lower electron affinity than H_2O; and (3) many stable hydroxy-bridged binuclear species are known in aqueous solution while stable aquo-bridged species are unknown. Relatively recently it has been pointed out that the case of cobalt(III) oxidants may be unique in that the cobalt(III)-bridging ligand bond may be greatly stretched in the activated complex[10a,16] so that the overall reaction energetics could require a relatively great reactivity for the hydroxy-bridged path.[17]

In striking contrast to the very high reactivity of hydroxy complexes in inner-sphere reactions, $Co(NH_3)_5OH^{2+}$ has been found to be less reactive than $Co(NH_3)_5OH_2^{3+}$ in outer-sphere reductions with $Ru(NH_3)_6^{2+}$ [15] and $Cr(bipy)_3^{2+}$.[14] On the basis of these limited observations it has been proposed[14,15] that the relative reactivities of hydroxy and aquo complexes might be useful criteria for distinguishing inner-sphere from outer-sphere electron-transfer reactions. Such criteria have been used to help clarify reactions of mechanistically ambiguous aquo ions.[18]

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We initiated the present study in order to examine the validity of these previous proposals concerning mechanistic significance of the relative reactivities of aquo and hydroxy complexes. We have chosen to use as oxidants cobalt(III) complexes containing the cyclic tetradentate ligands[19] (Figure 1) reported some time ago by Curtis.[20] These complexes are convenient for this study since both *trans*-Co(tet*a*)$(OH_2)OH^{2+}$ and *trans*-Co(*trans*[14]diene)$(OH_2)OH^{2+}$ are predominant species at conveniently low pH.[21] A more fundamental interest in these particular complexes in this study derives from the fact that hydrolysis of the cyclic ligands in such complexes, even with metals so labile as copper(II),[20] is necessarily slow and thus the corresponding $CoL(OH_2)_2{}^{3+,2+}$ couples should be reversible. Mechanistic studies involving such reversible reductions of cobalt(III) complexes are very rare. Since the cobalt(II) products of reaction can in principle be thoroughly characterized, reduction potentials of the cobalt(II)–cobalt(III) couples determined, etc., such studies should make possible a critical assessment of the validity of models which have been postulated to account for the reactivity patterns of cobalt(III) complexes.

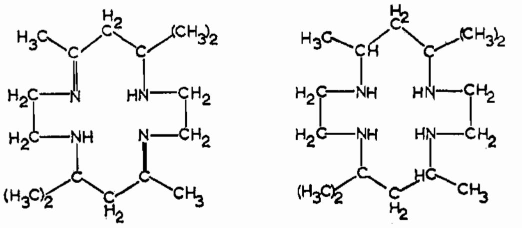
TRANS[14]DIENE TETA OR TETB

Figure 1.—Macrocyclic ligands.

Experimental Section

A. **Preparation of Complexes and Reagents.**—**[Co(*trans*[14]diene)(OH)$(C_2H_3O_2)$](ClO_4)** was prepared by dissolving (*trans*-[14]diene)·$2HClO_4$ (prepared as described elsewhere[22]) and an excess of cobaltous acetate in hot methanol until a reddish black solution was obtained. The solution was filtered and oxygen (or air) was bubbled through the filtrate until most of the supernatant liquid had departed. The solid was then recrystallized from water to obtain reddish black elongated crystals. Infrared and nmr spectra suggest that the axially coordinated ligands are hydroxide and acetate ion.[23] Elemental analysis was carried out by Galbraith Microanalytical Laboratory. *Anal.* Calcd for $[Co(C_{16}N_{32}N_4)(OH)(C_2H_3O_2)](ClO_4)$: C, 41.99; H, 7.04; N, 10.88; Cl, 6.88. Found: C, 41.73; H, 6.85; N, 9.71; Cl, 6.45.

When allowed to stand in a desiccator for several days, the crystalline solid disintegrates into a reddish gray powder. Disappearance of the band at 2.8 μ in the infrared spectrum suggests the loss of the hydroxide ligand, possibly due to the formation of a dimeric species with loss of water.

[*trans*-Co(*trans*[14]diene)$(OH_2)_2$]$(ClO_4)_3$.—Concentrated perchloric acid was added to solid samples[24] or concentrated solutions of Co(*trans*[14]diene)(OH)$(C_2H_3O)_2{}^+$ or Co(*trans*[14]-diene)CO_3.$^{+24,25}$ A dark green solid was obtained which was recrystallized from methanol, ethanol, or dilute perchloric acid. The two starting materials appear to yield the same product. The diaquo complex is hygroscopic and difficult to purify (the principal impurities are water and $HClO_4$). Analysis indicates that water of crystallization may be present. *Anal.* Calcd for $[Co(C_{16}H_{32}N_4)(H_2O)_2](ClO_4)$: C, 28.52; H, 5.39; N, 8.32; Cl, 15.79. Found: C, 27.85; H, 5.73; N, 7.69; Cl, 15.52.

[*trans*-Co(*trans*[14]diene)$(OH_2)(OH)$]$(ClO_4)_2$.—An aqueous solution of *trans*-Co(*trans*[14]diene)$(H_2O)_2{}^{3+}$ ($<3 \times 10^{-3}$ *M*) was brought to pH 5–7 with NaOH and allowed to stand. A dark red crystalline precipitate became visible in about 5 min and precipitation appeared complete after approximately 15–20 min. Since no precipitate could be obtained below pH 4 nor above pH 7, the solid which was isolated was assumed to be [Co-(*trans*[14]diene)$(OH_2)(OH)$]$[ClO_4)_2$.

Analysis by Spang Microanalytical Laboratory suggests that the complex contained water. *Anal.* Calcd for [Co(*trans*[14]-diene)$(OH_2)(OH)](ClO_4)_2 \cdot 2H_2O$: C, 31.4; H, 6.4; N, 9.2; Cl, 11.6. Found: C, 30.91; H, 6.05; N, 8.92; Cl, 11.38.

Although the analysis does not rule out the possibility that the precipitate is an oxy- or hydroxy-bridged dimer, the rapid rate of formation and precipitation is most consistent with a monomeric species. Further evidence comes from nmr studies which show that Co(*trans*[14]diene)$(OH_2)_2{}^{3+}$ and Co(*trans*[14]diene)$(OH)_2{}^+$ are formed when $HClO_4$ or NaOH, respectively, are added to solutions of the compound in D_2O. Co(*trans*[14]diene)$Cl_2{}^+$ is obtained (but more slowly) when HCl is added to the compound.

[Co(tet*a*)$(OH_2)OH$]$(ClO_4)_2$.—A brownish red solid was isolated from dilute solutions ($\geq 3 \times 10^{-4}$ *M*, in 1 *M* $NaClO_4$) of Co(tet*a*)$(OH_2)_2{}^{3+}$ when $3 < pH < 6$. The compound is probably [Co(tet*a*)$(OH_2)OH^{2+}$]$(ClO_4)_2$; however, the possibility that the solid is a dimer could not be ruled out. No further work was done on the compound due to its insolubility (solubility limit at 25° in 1 *M* $NaClO_4$ is approximately 2×10^{-4} *M*).

[Co(*trans*[14]diene)$(OH)_2$]ClO_4 and [Co(tet*a*)$(OH)_2$](ClO_4).—These complexes were prepared and studied in solution only. Aqueous solutions of Co(*trans*[14]diene)$(OH_2)_2{}^{3+}$ or Co(tet*a*)-$(OH_2)_2{}^{3+}$ were adjusted to the appropriate pH with NaOH.

Cobalt(II) Macrocyclic Complexes.—The cobalt(II) analogs of Co(*trans*[14]diene)$(OH_2)_2{}^{3+}$ and Co(tet*a*)$(OH_2)_2{}^{3+}$ were prepared in aqueous solution by reduction of the cobalt(III) complexes with excess Cr^{2+}, $Ru(NH_3)_6{}^{2+}$, or V^{2+}. Solutions of the Co(*trans*-[14]diene)$(OH_2)_2{}^{2+}$ are yellow and those of Co(tet*a*)$(OH_2)_2{}^{2+}$ are pink. Since both the cobalt(II) species and the reducing agents are oxygen sensitive, all solutions were kept under nitrogen. In some of our work, these cobalt(II) complexes were prepared by reducing the corresponding cobalt(III) complexes electrolytically. Solutions of the cobalt(III) complexes were deoxygenated and a controlled potential was applied for approximately 2 hr. The progress of the reduction was monitored by frequently checking the potential due to the Co^{3+}–Co^{2+} couple.

A yellow-brown solid was obtained as precipitate when a solution of [*trans*-Co(*trans*[14]diene)$(OH_2)_2$]$(ClO_4)_3$ was boiled in 95% ethanol for about 15 min. This solid, tentatively identified as [Co(*trans*[14]diene)]$(ClO_4)_2$, was filtered, washed with ethanol, and dried in a desiccator. This cobalt(II) complex is soluble in dilute $HClO_4$. When a portion of the acidic solution of this complex is added to a deoxygenated solution of $Co(NH_3)_5$-Br^{2+}, the violet color of the pentaammine complex fades slowly, consistent with the reduction of the pentaammine. When allowed to stand exposed to the air for several hours, the yellow solution of the solid cobalt(II) complex in dilute acid becomes progressively more green. This can be attributed to the oxidation of the yellow cobalt(II) species by oxygen to the green cobalt(III) complex.

Solutions of Reducing Agents.—Aqueous solutions of Cr^{2+} for use as reducing agent were prepared by dissolving a weighed amount of high-purity chromium metal (Johnson Matthey and Co., Ltd., London, England) in oxygen-free perchloric acid.[26] Alternatively, chromous solutions were produced by reducing a solution of $Cr(ClO_4)_3$ with amalgamated zinc in perchloric acid. A solution of $Cr(ClO_4)_3$ was obtained by reducing an acidic solution of recrystallized sodium dichromate with hydrogen peroxide.

The Cr^{2+} titer of reagent solutions was determined for all reductions where an excess of Cr^{2+} was used. A known volume of the Cr^{2+} solution was injected into an excess of $Co(NH_3)_5Br^{2+}$ in $HClO_4$. The concentration of the Cr^{2+} was determined from the change in absorbance at 2525 Å (for $Co(NH_3)_5Br^{2+}$, ε 1.67 ×

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(19) *trans*[14]diene = 5,7,7,12,14,14-hexamethyl-1,4,8,11, -tetraazacyclotetradeca-4,11-diene and tet*a* = 5,7,7,12,14,14-hexamethyl-1,4,7,11-tetraazacyclotetradecane.

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10^4) or from the amount of Co_{aq}^{2+} produced. In the latter case 4.0 ml of the product solution was added to 8.0 ml of 50% NaSCN and 13 ml of acetone. The concentration of the resulting thiocyanate complex was determined from the absorbance at 6200 Å (ϵ 1.82×10^3).[27]

Chromous solutions for scrubbing nitrogen were prepared by reducing commercial $Cr(ClO_4)_3 \cdot 6H_2O$ with amalgamated zinc in dilute $HClO_4$.

Hexaammineruthenium(III) perchlorate was prepared by dissolving a sample of commercial $Ru(NH_3)_6Cl_3$ (Johnson Matthey and Co., Ltd.) in water and adding a concentrated solution of sodium perchlorate until a white precipitate appeared. The first crop, which may contain a higher percentage of the chloropentaammine complex, was discarded. Successive crops of the white precipitate were collected, washed with dilute $NaClO_4$, and dried under suction.

Warning! Perchlorate salts of ruthenium ammines may be explosive when dry. A particularly bad explosion occurred in the present study during the recrystallization of a 1 month old sample of $[Ru(NH_3)_6](ClO_4)_3$. The recrystallized sample (~0.5 g) was collected on a fritted-glass funnel and washed with acetone before the explosion. It should be noted that $[Ru(NH_3)_6](ClO_4)_3$ reacts with acetone to form blue or black materials.[28] These substances have not been characterized.

Solutions of $Ru(NH_3)_6^{2+}$ for use as a reducing agent were prepared by reducing aqueous solutions of $Ru(NH_3)_6^{3+}$ with solutions of Cr^{2+} in dilute $HClO_4$. Since the Ru(II) species is oxidized by perchlorate ion in acidic solution,[29,30] solutions of $Ru(NH_3)_6^{2+}$ were freshly prepared within 5 min before each experiment.

Vanadyl perchlorate solutions were prepared by dissolving commercial $VOSO_4 \cdot xH_2O$ in dilute $HClO_4$ containing a very slight excess of barium perchlorate. Stock solutions of V^{2+} for use as reducing agent were prepared by reducing $VO(ClO_4)_2$ solutions over amalgamated zinc in 1–2 M perchlorate acid. The V^{2+} titer in the stock solutions was determined by injecting a known volume of the latter into an excess of $Co(NH_3)_5Br^{2+}$ in $HClO_4$ and allowing the reaction to proceed for 20 min. The concentration of cobalt(II) so produced was determined by the thiocyanate method.

Other Reagents.—Solutions of sodium perchlorate were prepared from primary standard Na_2CO_3 and reagent grade $HClO_4$. Lithium perchlorate was obtained from reagent grade Li_2CO_3 and $HClO_4$. Solutions of both $NaClO_4$ and $LiClO_4$ were standardized by passing well-diluted aliquots through a cation-exchange column (Dowex 50W-X2, 20–50 mesh, H^+ form) and titrating the eluted acid with standard NaOH. All solutions were prepared with deionized, distilled water. All other chemicals were of reagent grade and were used without further purification.

B. Physical Properties of the Macrocyclic Complexes.—1. **Infrared spectra** were obtained from Nujol mulls of solid samples using Perkin-Elmer Models 137 and 237 spectrophotometers. Spectra of the complexes used in this study were in agreement with literature reports.[24,25]

2. **Ultraviolet and visible spectra** of aqueous solutions were determined using a Cary Model 14 or 16 or the Unicam SP800A spectrophotometer. Solutions of all aquohydroxy and dihydroxy species were obtained by adjusting solutions of the corresponding diaquo complexes to the appropriate pH. Spectra of *trans*-Co(*trans*[14]diene)X_2^{n+} and *trans*-Co(teta)X_2^{n+} (X = OH_2, OH) were in agreement with literature reports.[24,25]

C. Acid Dissociation Constants.—Constants for dissociation of the acidic protons of the diaquo complexes *trans*-CoL$(OH_2)_2^{3+}$

$$\textit{trans}\text{-CoL}(OH_2)_2^{3+} \rightleftharpoons \textit{trans}\text{-CoL}(OH_2)(OH)^{2+} + H^+ \qquad K_1$$

$$\textit{trans}\text{-CoL}(OH_2)(OH)^{2+} \rightleftharpoons \textit{trans}\text{-CoL}(OH)_2^{+} + H^+ \qquad K_2$$

were determined by titrating weighted samples of the complexes with standard NaOH. All solutions were prepared at 1.0 M ionic strength ($NaClO_4$) and thermostated to 25°. pH measurements were made using a Beckman Zeromatic pH meter and a Beckman No. 39142 glass–Ag–AgCl combination electrode. The instrument was standardized against standard buffer solutions of pH 6.86 and 4.01. Due to the high concentration of sodium ions, the glass electrode was unreliable above pH 7 and almost completely unresponsive above pH 9.

The pK_1 values for the complexes were determined from the midpoints of the buffered regions. The pK_2 for *trans*-Co(*trans*-[14]diene)$(OH_2)_2^{3+}$, which could not be directly determined due to sodium ion errors at higher pH, was estimated by assuming that the pH at the stoichiometric end point for the titration of the first proton was equal to $^1/_2$(pK_1 + pK_2).

Results of these measurements are given in Table I. The pK values for the diaquo complexes are compared to those obtained by Kernohan[21,24] from titrations where the ionic strength was not controlled. It is to be noted that pK values reported in Table I are mixed concentration–activity constants.

TABLE I

ACID DISSOCIATION CONSTANTS[a] FOR *trans*-CoL$(OH_2)_2^{3+}$

Complex	pK_1[b]	pK_2[b]	No. of determinations
Co(*trans*[14]diene)-$(OH_2)_2^{3+}$	4.02 ± 0.01 (4.02 ± 0.01)	8.4 ± 0.2[c] (8.2 ± 0.1)	2
Co(teta)$(OH_2)_2^{3+}$	2.70 (2.70 ± 0.05)	6.8 (6.40 ± 0.05)	1

[a] Ionic strength maintained constant at 1.0 M ($NaClO_4$); temperature 25° Since pK_1 was determined as equal to the measured pH at which $[CoL(OH_2)_2^{3+}] = [CoL(OH_2)OH^{2+}]$, constants are mixed activity–concentration constants. [b] Values in parentheses are from ref 24 at 25°; ionic strength not controlled. [c] Estimated (see text).

An attempt was made to determine the acid dissociation constants for Co(*trans*[14]diene)$(OH_2)_2^{2+}$ and Co(teta)$(OH_2)_2^{2+}$. The cobalt(II) complexes were prepared by applying a controlled potential (ATR rectifier power supply, Model 610-C-ELIF) across solutions of the respective cobalt(III) complexes until reduction was complete. The progress of the reduction was monitored by frequent readings of the Co(II)–Co(III) redox potential (for details seen ref 23) of the electrolyzed solution. The ionic strength was not controlled in these experiments due to the insolubility of the cobalt(II) complexes at high $[ClO_4^-]$. Once prepared, the solutions of the cobalt(II) complexes were titrated with standard NaOH as described above. Plots of the pH *vs.* volume of NaOH exhibit no buffered regions below pH 9. This indicates that the pK values are greater than 9. Since the axial water molecules must be very weakly bound to be so weakly acidic, the coordination number of these cobalt(II) complexes must be regarded as unknown. Spectral and magnetic studies of these cobalt(II) complexes in aqueous solution have been cited as evidence of a very large tetragonal distortion.[31] Similar uncertainties with regard to the axial coordination positions also occur in solutions of the nickel(II) and copper(II) complexes with the Curtis ligands.[20,32] In view of the uncertainties we feel that it is better to refer to the aqueous species as Co(*trans*[14]diene)$^{2+}$ (by analogy with the copper(II) and nickel(II) complexes) rather than *trans*-Co(*trans*[14]diene)$(OH_2)_2^{2+}$. However, for the sake of brevity, we will formulate the reduced species as Co(*trans*[14]-diene)$(OH_2)_2^{2+}$ in the context of the reversible electrode reactions; this formulation is intended only to acknowledge the reaction stoichiometry and the fact that solvent molecules must be in the neighborhood of the axial coordination positions, even if at a distances greater than normally considered bonding.

D. Oxidation Potentials.—The oxidation potentials of the Co(*trans*[14]diene)$(OH_2)_2^{2+,3+}$ and Co(teta)$(OH_2)_2^{2+,3+}$ couples were determined with an Instrumentation Laboratories Model 145 pH meter using saturated calomel and platinum gauze electrodes. A solution of the cobalt(III) complex was placed in the reaction compartment, thermostated to 25.0°, and deoxygenated by bubbling nitrogen through the cell. A solution of Cr^{2+} of the same pH and ionic strength was then injected in small aliquots from a 1-ml graduated syringe. The potential was measured after each aliquot was added. The correction factor for the potential, due to the saturated calomel electrode (−0.242 V at

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(27) V. M. Zvenigorodskaya, "Colorimetric Methods of Analysis," Vol. II, F. T. Snell and C. T. Snell, Ed., 3rd ed, Van Nostrand New York, N. Y., 1959, p 362.

(28) J. F. Endicott, unpublished observations.

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(31) L. Warner, Ph.D. Dissertation, Ohio State University, 1968.

(32) J. M. Palmer, E. Papaconstantinou, and J. F. Endicott, *Inorg. Chem.*, **8**, 1516 (1969).

25°[33]) and to the liquid junction potentials, was determined by measuring the formal potential of the Fe(II)–Fe(III) couple at 1.0 *M* ionic strength and comparing this value to the accepted literature value. A solution of $Fe(NH_4)(SO_4)_2$ in 0.6 *M* $HClO_4$ and 1.0 *M* ionic strength ($HClO_4$, $NaClO_4$) was reduced by Cr^{2+} as described above. Under these conditions of acidity and ionic strength the hydrolysis of the ferric ion is negligible.[34] The potential of the Fe(II)–Fe(III) couple was determined from a plot of the observed potential *vs.* volume of titrant. A value of −0.497 V (Latimer convention) was read for the potential at half-equivalence. A second value, −0.488 V, was obtained by mixing equimolar solutions of $FeNH_4(SO_4)_2$ and $Fe(NH_4)_2(SO_4)_2$ (in 0.6 *M* $HClO_4$, 0.4 *M* $NaClO_4$) and measuring the potential of the resulting solution. The average of these two values, −0.492 V, was subtracted from the literature value, −0.741 V,[35] to give a cell correction factor of −0.249 V.

The oxidation potential of the Co(*trans*[14]diene)$(OH_2)_2^{3+,2+}$ couple was measured at both 1.0 and 0.1 *M* ionic strengths. Since the difference between the measured potentials at the two ionic strengths was within the experimental error (±10 mV), the same cell correction was applied. The potential of the Co(teta)$(OH_2)_2^{3+,2+}$ couple was determined at 0.1 *M* ionic strength only, due to the insolubility of the Co(II) complex at higher ionic strengths.

E. **Techniques.**—All reactions with second-order rate constants $\geq 10^4\ M^{-1}\ sec^{-1}$ were studied using the stopped-flow technique. Details of methods and apparatus used have been fully described in ref 36. The functioning of the stopped-flow apparatus was checked by observing the rate of reduction of 3.00×10^{-3} *M* $Co(NH_3)_5(OH_2)^{3+}$ by 4.75×10^{-2} *M* Cr^{2+} at pH 1.0. The reaction was observed at 3450 Å, at $\mu = 1.0$ *M* ($HClO_4$, $NaClO_4$), and at 25°. Under these conditions all absorbance changes were attributed to $Co(NH_3)_5(OH_2)^{3+}$ (ϵ_{3450} 44.1[37]). A second-order rate constant, $k_{obsd} = 21.5\ M^{-1}\ sec^{-1}$, was calculated from six determinations. This value compares well with the value $k_{obsd} = 22.5\ M^{-1}\ sec^{-1}$ obtained from the data of Zwickel and Taube ($\mu = 1.2$ *M;* extrapolated to 25°).[10b,14,37]

Slower reactions, including all reductions by $Ru(NH_3)_6^{2+}$ and V^{2+} were studied using the Cary Model 14 recording spectrophotometer. Details of the spectrophotometric and syringe techniques have been described elsewhere.[15,17,36,38]

Reactions where Co(*trans*[14]diene)$(OH_2)_2^{3+}$ was the oxidant were monitored at 2750 Å; those with Co(teta)$(OH_2)_2^{3+}$, at 2600 Å. Spectral data for all reactants and products at these wavelengths are given in Table II.

TABLE II

MOLAR EXTINCTION COEFFICIENTS OF REACTANTS AND PRODUCTS

Absorption species	Molar extinction coeff 2600 Å	Molar extinction coeff 2750 Å
trans-Co(*trans*[14]diene)$(OH_2)_2^{3+}$	1.43×10^4	1.02×10^4
trans-Co(*trans*[14]diene)$(OH_2)(OH)^{2+}$	1.25×10^4	0.71×10^4
trans-Co(*trans*[14]diene)$(OH)_2^{+}$		0.65×10^4
Co(*trans*[14]diene)$^{2+}$	1.00×10^3	1.10×10^3
trans-Co(teta)$(OH_2)_2^{3+}$	1.60×10^4	
trans-Co(teta)$(OH_2)(OH)^{2+}$	1.27×10^4	
trans-Co(teta)$(OH)_2^{+}$	1.10×10^4	
Co(teta)$^{2+}$	1.47×10^2	
Cr_{aq}^{2+}	100	25
Cr_{aq}^{3+}	200	110
$Ru(NH_3)_6^{2+}$	6.60×10^2	624 ± 10[a]
$Ru(NH_3)_6^{3+}$	4.01×10^2	465 ± 10[a]
V_{aq}^{3+}	1.0[b]	0.1[b]

[a] In 0.1 *M* $NaClO_4$: T. J. Meyer and H. Taube, *Inorg. Chem.*, **7**, 2369 (1968). [b] S. C. Furman and C. S. Garner, *J. Amer. Chem. Soc.*, **72**, 1785 (1950).

Because of the sensitivity of the reactants and products to oxygen, all experiments were performed under an atmosphere of scrubbed nitrogen. Solutions were transferred by means of gastight glass syringes equipped with platinum needles.

The pH of the solutions was adjusted with $HClO_4$ or NaOH and was determined by dilution or by direct measurement of the product solutions using a Beckman Zeromatic pH meter. The ionic strength was maintained with $LiClO_4$ or $NaClO_4$. For reductions using Cr^{2+} or V^{2+} as reducing agents, the ionic strength was held at 1.0 *M*. In $Ru(NH_3)_6^{2+}$ reductions the ionic strength was 0.1 *M*. All work was done at 25°.

Stock solutions of the cobalt(III) complexes were prepared in 0.1 *M* $HClO_4$ in order to minimize dimerization. Known quantities of the stock solution were injected into solvents of the appropriate pH and ionic strength immediately before experiments were begun. In experiments conducted on the Cary 14 (all $Ru(NH_3)_6^{2+}$ and V^{2+} reactions) reaction solutions of approximately 10^{-5} *M* Co(III) were prepared and used within 10 min. Under these conditions there was no possibility of significant dimer formation. In stopped-flow experiments (where several runs were obtained using the same cobalt(III) solution) $\leq 2 \times 10^{-4}$ *M* cobalt(III) solutions were prepared and all experiments were performed within 1 hr. During this time the absorbance of the cobalt(III) solution was checked regularly. In all cases, this absorbance and presumably the concentration of the monomeric species remained essentially constant within experimental error (note that the rate of formation of dimer under these conditions should be $<8 \times 10^{-6}\ M\ hr^{-1}$).

The initial concentration of the cobalt(III) species in the reaction was calculated from dilution or from the absorbance of the solution at zero time. In some $Ru(NH_3)_6^{2+}$ reductions a portion of the cobalt(III) complex was first reduced by the excess Cr^{2+} present in the system. The corrected initial concentration of the Co(III) species in the Co(III)–$Ru(NH_3)_6^{2+}$ reaction was obtained from

$$[Co(III)]_{0_{cor}} = [Co(III)]_0 - [Cr^{2+}]_0$$

In some experiments the initial cobalt(III) concentration was varied over a tenfold range at constant pH. The treatment of kinetic data has been described elsewhere[17,36,39] and as in a previous study[39] we have found it useful to check the validity of calculated second-order rate constants from the stopped-flow work using a pseudo-first-order treatment.[39]

All such calculations were made on the basis of the rate law

$$\text{rate} = k[Co(III)][Red]$$

where

$$[Co(III)] = [CoL(OH_2)_2] + [CoL(OH_2)(OH)] + [CoL(OH)_2]$$

An experimentally determined composite extinction coefficient for Co(III) was obtained for each pH. However, since the reactivity of the diaquo complex differs significantly from that of the aquohydroxy complex, it is more useful to express the rate equation as

$$\text{rate} = k'[CoL(OH_2)_2^{3+}][Red]$$

The value of k' is then obtained from

$$k' = k(K_1K_2 + K_1[H^+] + [H^+]^2)[H^+]^{-2} \qquad (1)$$

where K_1 and K_2 are constants for the dissociation of the first and second protons of $CoL(OH_2)_2^{3+}$. When the pH of the solution is well below the pK_2 of the oxidant, eq 1 reduces to

$$k' = k(1 + K_1/[H^+]) \qquad (2)$$

In Co(III)–$Ru(NH_3)_6^{2+}$ reactions the rate law may be expressed

$$\text{rate} = k''[CoL(OH_2)(OH)^{2+}][Ru(NH_3)_6^{2+}]$$

in which case k'' can be calculated from

$$k'' = k(K_1K_2 + K_2[H^+] + [H^+]^2)/[H^+]K_1 \qquad (3)$$

of, if pH ≪ pK_2, from

$$k'' = k(1 + [H^+]/K_1) \qquad (4)$$

Determination of Dimerization Constants.—The dimerization constant, K_D, was determined from the initial rates of the forward and reverse polymerization reaction of *trans*-Co(*trans*[14]-diene)$(OH_2)OH^{2+}$.

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(35) W. C. Schumb, M. S. Sherrill, and S. B. Sweatser, *ibid.*, **59**, 2360 (1937).

(36) R. C. Patel, Ph.D. Dissertation, Boston University, 1969.

(37) A. Zwickel, Ph.D. Dissertation, University of Chicago, 1959.

(38) G. Svatos and H. Taube, *J. Amer. Chem. Soc.*, **83**, 4172 (1961).

(39) R. C. Patel, R. E. Ball, J. F. Endicott, and R. G. Hughes, *Inorg. Chem.*, **9**, 23 (1970).

Solutions of Co(*trans*[14]diene)$(OH_2)OH^{2+}$ were prepared by adjusting solutions of the diaquo complex to pH ≥ 4.8 with dilute NaOH. Progress of the reactions was monitored by observing changes in the absorbance at 5000 Å using a Cary Model 16 or 14 spectrophotometer. All work was done at 1.0 *M* ionic strength ($HClO_4$, $NaClO_4$) and 25°. pH measurements were made using a Beckman Zeromatic pH meter equipped with a Beckman No. 41263 glass electrode and a saturated calomel electrode.

In one case, the components of an equilibrated solution of Co(*trans*[14]diene)$(OH_2)(OH)^{2+}$ were separated on a Na^+-exchange resin and their spectra were recorded. An 8×10^{-4} *M* solution of the aquohydroxy complex, initial pH 6.3, was allowed to stand for 24 hr. The solution was then passed through a column of cation-exchange resin (Bio-Rad AG 50W-X_2, 200–400 mesh, Na^+ form). The first band, which appeared light pink and was presumably the monomer, was eluted with 0.2 *M* $Mg(ClO_4)_2$ and the exit solution was collected into dilute $HClO_4$. The concentration of the monomer as Co(*trans*[14]diene)$(OH_2)_2{}^{3+}$ was determined from the absorbance at 5800 Å (ϵ 27.4). The second (and last) band, which was orange-brown and was assumed to contain only dimer, was eluted with 2.0 *M* $Mg(ClO_4)_2$. The absorbance of the solution at 5000 Å was measured and the extinction coefficient for the dimer was calculated to be 1.3×10^2 ([dimer] = $^1/_2\{[Co(III)]_{total} - [monomer]\}$). Although some polymeric species were undoubtedly present in the second eluted band, the error in the calculated value of ϵ at 5000 Å is probably small as the absorbance per cobalt unit at 5000 Å appears to be similar for both the dimeric and polymeric species.

Assuming that the formation of dimer is second order with respect to the [Co(III)] (*i.e.*, before polymerization becomes important), we have the equation

$$\frac{1}{C} - \frac{1}{C_0} = k_f t \qquad (5)$$

where C_0 is the initial concentration of the monomer, C is the monomer concentration at time t, and k_f is the second-order rate constant for dimer formation. The observed absorbance, A, is due to the sum of the absorbance of the monomer and dimer

$$A = p\epsilon_M C + p\epsilon_D \frac{(C_0 - C)}{2}$$

where p is the optical path, ϵ_M is the molar extinction coefficient at 5000 Å of the monomer (35), and ϵ_D is ϵ_{5000} for the dimer (1.3×10^2). Therefore, for a reaction in a 10-cm cell

$$C = \frac{A - 650C_0}{-300}$$

Substituting in (5) gives

$$\frac{-1}{A - 650C_0} = \frac{k_f}{300}t + \text{constant}$$

A plot of $-(A - 650C_0)^{-1}$ *vs.* time for the dimerization reaction is linear. For example at pH 5.05, 25°, with the initial [*trans*-Co(*trans*[14]diene)$(OH_2)_2{}^{3+}$] = 0.97×10^{-3} *M* and at unit ionic strength we find

$$\frac{-1}{A_0 - 650C_0} = 2.39 \times 10^{-2}t - 3.48$$

First-order rate constants, k_d, for the dissociation of the dimer were calculated from spectral changes following acidification of solutions containing dimers. Plots of log $(A - A_\infty)$ *vs.* time (where A_∞ was a calculated value obtained from $A_\infty = p\epsilon_M C_0$) clearly show that at least two reactions of different rates occur (Figure 2). A value for the final absorbance of the first observed reaction, A_∞', can be obtained by extrapolating the latter portion of the curve to zero time (the same value of A_∞' is obtained by similarly extrapolating the final slope of a plot of absorbance *vs.* time). A plot of log $(A - A_\infty')$ *vs.* time for this reaction gives $k_d = 1.83 \times 10^{-4}$ sec^{-1}.

Results

1. Formal Reduction Potentials of Co^{III}–Co^{II} Couples.—The formal reduction potentials of the Co(*trans*[14]diene)$(OH_2)_2{}^{3+,2+}$ and Co(teta)$(OH_2)_2{}^{3+,2+}$ couples were found to be 0.560 and 0.592 V, respectively (Table III). This is consistent with the observation that I^- equilibrates with the cobalt(III) complexes and $I_3{}^-$.[40]

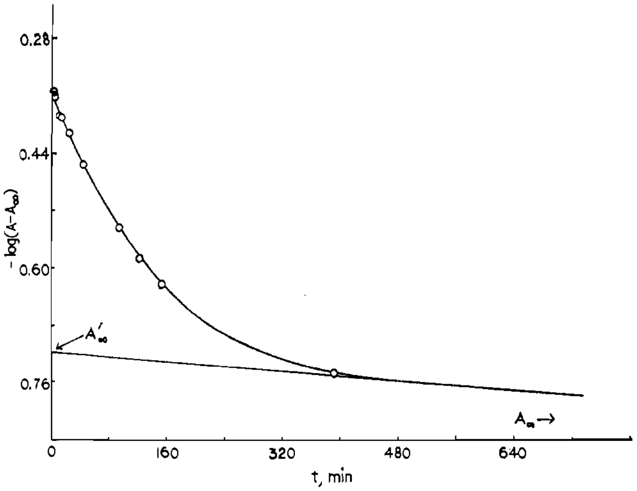

Figure 2.—Acid decomposition of the $\{H_2OCo($*trans*$[14]diene\}_2$-O^{4+} dimer and higher polymer at total [Co(III)] = 0.973×10^{-3} *M;* initial pH 1.8; μ = 1.0 *M;* 25°. Straight line shows limiting slope of the decay curve. Absorbances for a 10-cm path length.

TABLE III

FORMAL REDUCTION POTENTIALS OF Co(III)–Co(II) COUPLES AT 25.0°

Couple	$[H^+]$, *M*	Ionic strength, *M* ($NaClO_4$, $HClO_4$)	$E°$,[a] V
Co(*trans*[14]diene)$(OH_2)_2{}^{3+,2+}$	0.60	1.0	0.551
	0.30	1.0	0.554
	0.10	1.0	0.564
	0.10	0.1	0.557
Co(teta)$(OH_2)_2{}^{3+,2+}$	0.10	0.1	0.593
	0.10	0.1	0.590

[a] Formal potential of the Fe(II)–Fe(III) couple at μ = 1.0 *M* ($HClO_4$) used as reference (see text).

2. Dimerization Constants.—We have found that the visible spectra of aqueous solutions of *trans*-Co(*trans*[14]diene)$(OH_2)(OH)^{2+}$ undergo significant changes over a period of several hours while spectra of the corresponding diaquo and dihydroxy species appear to be stable. The spectral changes occur in a stepwise manner (see Figure 2). The first step may be attributed to the formation of a dimer. Subsequent changes are probably due to the formation of a polymeric species. Since some unusual acid-dependent reactivities have been observed in this study, we have carefully examined these dimerization reactions to ascertain whether they can complicate the electron-transfer studies.

If a solution of the aquohydroxy complex, "equilibrated" at pH 5, is made acidic (pH ≤ 3), the absorbance at 5000 Å is observed to decrease at three different rates. The initial drop in absorbance is too rapid to be followed by conventional spectrophotometric means and is attributed to the titration of the monomer. The first observable change, the initial, steep portion of the curve in Figure 2, is attributed to the dissociation of the dimer; the subsequent, slower change is attributed to the decomposition of the polymeric species.[41]

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[40] J. A. Kernohan, unpublished observations.

[41] Note that Figure 2 and our estimate of the molar absorptivity of the dimer may be used to set a lower limit for the dimerization constant at pH 5: $K_D = [(H_2OCoL)_2O^{4+}]/[CoL(OH_2)OH^{2+}]^2 > 10^4\ M^{-1}$. This limit was set using A_∞ to make a crude estimate of the minimum extent of polymerization.

Relatively small pH changes take place in the course of both the forward and reverse reactions (Table IV).

Results of dimer decomposition experiments (Table V) clearly indicate that the reverse reaction is acid dependent. The rate may be expressed as

TABLE IV

OBSERVED pH CHANGES DURING FORMATION AND DISSOCIATION OF DIMERIC–POLYMERIC SPECIES[a] OF $\mathrm{Co^{III}}$–*trans*[14]diene COMPLEXES

Time, hr	pH	A_{5000}	Time, hr	pH	A_{5000}
A. Formation of Dimer–Polymers					
0.00	6.3	$(0.379)^b$	35.10	5.78	0.5877
1.75	6.2	0.4317	96.00	5.75	0.6404
18.50	5.88	0.5600			
B. Dissociation of Dimer–Polymers					
0.00	2.90	$(0.488)^b$	48.00	3.30	0.3868
12.75	3.15	0.4601			

[a] Total Co(III) concentration 0.84×10^{-3} *M;* 1.0 *M* ionic strength ($NaClO_4$, $HClO_4$); 25°. [b] Estimated from extrapolation to zero time.

TABLE V

KINETIC DATA FOR THE DIMERIZATION OF *trans*-Co(*trans*[14]diene)OH_2OH^{2+}

A. Formation of Dimer[a]

Initial pH[b]	$[H^+]$, *M*	$10^3[\mathrm{Co(III)}]$,[c] *M*	10^2k_f,[d] $M^{-1}\,\mathrm{sec}^{-1}$
4.9	1.2×10^{-5}	0.890	2.38
5.0	1.0×10^{-5}	0.837	2.58
5.05	8.9×10^{-6}	0.973	2.38
6.2	6.3×10^{-7}	0.841	1.42

B. Dissociation of Dimer[a]

Time allowed for dimerizn, days	Initial pH	$10^3[\mathrm{Co(III)}]$,[c] *M*	10^4k_d,[f] sec^{-1}	$10k_r$,[g] $M^{-1}\,\mathrm{sec}^{-1}$
2	2.9^b	0.841	0.627	0.498
4	1.8^b	0.973	1.83	0.116
1	0.44^e	1.08	57.5	0.160
3	0.44^e	1.08	46.3	0.126
4	0.44^e	1.08	39.2	0.109
5	0.44^e	1.08	43.8	0.122

C. Estimated Per Cent Dimerization after 1 hr at $[\mathrm{Co(III)}] = 2.0 \times 10^{-4}\ M^{a,c}$

pH	$[\mathrm{CoL(OH_2)(OH)}]$,[h] *M*	$k_f[\mathrm{CoL(OH_2)(OH)}]^2$,[d] sec^{-1}	$[\mathrm{Co(III)}]^c$ which dimerized in 1 hr, *M*	% Co(III) as dimer
1	2.0×10^{-7}	3.5×10^{-8}	7.0×10^{-8}	0.04
2	2.0×10^{-6}	3.5×10^{-7}	7.0×10^{-7}	0.35
3	1.8×10^{-5}	2.8×10^{-6}	5.6×10^{-6}	2.8
4	1.0×10^{-4}	8.6×10^{-6}	1.7×10^{-5}	8.5
5	1.8×10^{-4}	2.8×10^{-6}	5.6×10^{-6}	2.8
6	2.0×10^{-4}	3.5×10^{-7}	7.0×10^{-7}	0.35

[a] $\mu = 1.0$ *M* ($HClO_4$, $NaClO_4$), 25.0°. [b] Measured. [c] [Co(III)] is the total concentration of all cobalt(III) species. [d] $d[\mathrm{dimer}]/dt = k_f[\mathrm{CoL(OH_2)(OH)}]^2$. [e] Calculated from dilution. [f] $-d[\mathrm{dimer}]/dt = k_d[\mathrm{dimer}]$. [g] $k_r = k_d/[H^+]$. [h] $[\mathrm{CoL(OH_2)(OH)}] = [H^+]/([H^+] + K_1)[\mathrm{Co(III)}]$.

$$\frac{-d[\mathrm{dimer}]}{dt} = \frac{1}{2}\,\frac{d[\mathrm{Co}(\mathit{trans}[14]\mathrm{diene})(\mathrm{OH_2})_2{}^{3+}]}{dt} = k_d[\mathrm{dimer}]$$

In the range pH < pK_1, the dissociation of the dimer may be described by a two-step mechanism[42]

$$\mathrm{H_2O + (H_2OLCoL)_2O^{4+} + H^+ \overset{k_r}{\rightleftharpoons} CoL(OH_2)_2{}^{3+} + CoL(OH_2)(OH)^{3+}} \quad \text{(slow)}$$

$$\mathrm{CoL(OH_2)(OH)^{2+} + H^+ \rightleftharpoons CoL(OH_2)_2{}^{3+}} \quad \text{(fast)}$$

Presumably the rate of the forward reaction, the formation of the dimer, must also be H^+ dependent. However our present results indicate that the stoichiometry of formation is given by[42]

$$\mathrm{2CoL(OH_2)(OH)^{2+} \rightleftharpoons (H_2OCoL)_2O^{4+} + H_2O} \qquad (6)$$

Since the formation rate is given by $k_f[\mathrm{CoL(OH_2)OH}]^2$ at pH 5 (Table VI), then

$$K_D = \frac{[\mathrm{(H_2OCoL)O_2{}^{4+}}]}{[\mathrm{CoL(OH_2)(OH)^{2+}}]^2} = \frac{k_f}{k_d'} \leq 2 \times 10^5\ M^{-1}$$

where $k_d' > 1.2 \times 10^{-7}\ \mathrm{sec}^{-1}$ is the specific rate constant for decomposition of the dimer, extrapolated to pH 5.0.[43]

Visible spectra indicate that the Co(tet*a*)(OH_2)(OH)$^{2+}$ complex dimerizes in an analogous way. However, a complete study of its behavior was not possible due to the low solubility of the aquohydroxy species. An attempt was made to observe dimerization using cobalt(III) concentrations $\leq 10^{-4}$ *M*. Under these conditions the reaction proceeds so slowly ($t_{1/2} \gg 12$ hr) that the decomposition of the entire macrocyclic structure ($\mathrm{Co(OH_2)_6{}^{2+}}$ can be detected by extraction of the thiocyanate complex) becomes important before a significant amount of dimer has been formed.

3. Electron-Transfer Studies.—All the observed reactions obeyed second-order kinetics. This is demonstrated by the linearity of the second-order plots $\ln A_t/(A_t - A_\infty)$ *vs.* time and is further supported by the agreement between values of the rate constant obtained from second-order and pseudo-first-order treatments of the experimental data and in some cases by the concentration independence of the calculated rate constants.

The Cr^{2+} Reductions of *trans*-$\mathbf{CoL(OH_2)_2{}^{3+}}$.—The rate of the Cr^{2+} reduction of the diaquocobalt(III) complexes may be expressed as

$$\mathrm{rate} = k'[\mathrm{CoL(H_2O)_2{}^{3+}}][\mathrm{Cr^{2+}}]$$

Values of k' for the Co(*trans*[14]diene)$(H_2O)_2{}^{3+}$–Cr^{2+} and Co(tet*a*)$(H_2O)_2{}^{3+}$–Cr^{2+} systems are presented in Table VI.

The $\mathbf{Ru(NH_3)_6{}^{2+}}$ Reductions of *trans*-$\mathbf{CoL(OH_2)_2{}^{3+}}$.—We have found that the rates of the ruthenium(II) reductions of the $\mathrm{CoL(OH_2)_2{}^{3+}}$ complexes increase with $[H^+]$. This increase is approximately linear if the rate law is expressed in terms of $[\mathrm{CoL(OH_2)OH^{2+}}]$

$$\frac{d[\mathrm{Co(III)}]}{dt} = -k''[\mathrm{CoL(OH_2)OH^{2+}}][\mathrm{Ru(NH_3)_6{}^{2+}}]$$

Our determinations of k'' for L = tet*a* and *trans*[14]-diene are summarized in Figures 3 and 4.

Scatter in the results of the Co(tet*a*)(OH_2)(OH)$^{2+}$–$\mathrm{Ru(NH_3)_6{}^{2+}}$ reactions is attributed to the sensitivity of k'' to errors in the value of $[\mathrm{Co(III)}]_\infty$. The final concentration of the oxidant was obtained from the initial cobalt(III) concentration and the change in absorbance during the reaction. Since in these experiments the reduction by $\mathrm{Ru(NH_3)_6{}^{2+}}$ was preceded by the re-

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[42] Although we have no direct structural evidence, we have formulated the dimer as oxy bridged rather than dihydroxy bridged since the latter would involve folding the very bulky macrocyclic ligands. Complexes with the teta ligand folded have not been identified;[20] the *trans*[14]diene ligand can be trapped in a folded configuration,[20,25] but this is clearly an unstable arrangement[20] (see also J. A. Kernohan and J. F. Endicott, *J. Amer. Chem. Soc.*, **91**, 6977 (1969)).

[43] We have taken $1.2 \times 10^{-7}\ \mathrm{sec}^{-1}$ to be the lower limit of k_d at pH 5 since k_f may be only weakly acid dependent at pH 5 (see Table V). We have used this upper limit of $K_D = 2 \times 10^5\ M^{-1}$ in the analysis of the significance dimerization since for our purposes it is essential to estimate the maximum possible extent of dimerization.

TABLE VI

CHROMIUM(II) REDUCTIONS OF *trans*-$CoL(OH_2)^{3+}$ COMPLEXES

$[H^+]$, M	$1/[H^+]$, M^{-1}	$(1 + K_1)/[H^+]$	$10^4[Co(III)]$,[a] M	$10^4[Cr(II)]_{init}$, M	$10^{-3}k$, $M^{-1}\ sec^{-1}$	$10^{-3}k'$, $M^{-1}\ sec^{-1}$
L = *trans*[14]diene						
0.915	1.09	1.000	0.170	0.141	0.36	0.36
0.762	1.31		0.176	0.111	0.43	0.43
0.611	1.64		0.190	0.131	0.59	0.59
0.459	2.18		0.199	0.140	0.69	0.69
0.385	2.60		0.175	0.175	0.96	0.96
0.383	2.61		0.176	0.124	0.93	0.93
0.309	3.24		0.165	0.093	1.01	1.01
0.307	3.26		0.177	0.113	1.06	1.06
0.230	4.35		0.822	0.0442	2.25	2.25
0.229	4.37		0.888	0.0330	2.65	2.65
0.191	5.24	1.001	0.0903	0.0353	2.94	2.95
0.153	6.54		0.0983	0.0342	2.90	2.91
0.115	8.70		0.0960	0.0460	3.53	3.53
0.111	9.01		0.0852	0.0250	3.00	3.00
0.077	13.0		0.0842	0.0513	4.7	4.7
0.074	13.5		0.0873	0.0463	4.8	4.8
0.063[b]	15.8	1.002	0.885	0.573	5.2	5.3
0.039	25.6	0.98	0.0863	0.0531	7.8	7.9
0.010	0.100	1.010	0.972	0.79 ± 0.09[c]	21 ± 2[c]	21 ± 1[c]
8.91×10^{-3}	112	1.011	1.47	0.68 ± 0.00[d]	22 ± 2[d]	22 ± 2[d]
7.08×10^{-3}	141	1.014	1.02	0.56 ± 0.05[e]	16 ± 3[e]	16 ± 3[e]
6.31×10^{-3}	158	1.016	0.916	0.70 ± 10[e]	29 ± 6[e]	30 ± 6[e]
6.17×10^{-3}	162	1.016	1.47	0.40 ± 0.02[d]	23 ± 0[d]	24 ± 0[d]
			1.39	0.19 ± 0.01[d]	22 ± 3[d]	22 ± 3[d]
4.57×10^{-3}	219	1.022	1.00	0.69 ± 0.20[g]	35 ± 5[g]	36 ± 5[g]
3.98×10^{-3}	251	1.025	2.60	0.82 ± 0.01[e]	32 ± 1[e]	33 ± 1[e]
2.00×10^{-3} [b]	500	1.050	1.10	0.85	53	56
1.00×10^{-3} [b]	1000	1.100	1.00	0.65 ± 0.15[e]	114 ± 51[e]	125 ± 56[e]
8.91×10^{-4}	1120	1.112	0.833	0.662	154	172
				0.42 ± 0.01[e]	123 ± 2[e]	136 ± 2[e]
2.2×10^{-6}	4.46×10^5	45.9	0.883	0.50 ± 0.01[e]	854 ± 77[e]	$(3.9 \pm 0.4) \times 10^4$ [e]
L = teta						
1.005	0.995	1.002	1.507	0.99 ± 0.01[d]	14[d]	14[d]
0.700	1.43	1.003	0.834	0.61	16	16
0.500	2.00	1.004	0.872	0.32	26	26
0.300	3.33	1.007	1.027	0.73 ± 0.08[d]	46[d]	46[d]
0.202	4.95	1.010	0.951	0.47 ± 0.01[d]	70 ± 10[d]	71 ± 13[d]
0.154	6.49	1.013	0.803	0.39 ± 0.12[d]	68 ± 13[d]	68 ± 14[d]
0.102	9.80	1.020	0.752	0.35 ± 0.01[d]	97 ± 5[d]	99 ± 5[d]
0.078	12.82	1.026	0.958	0.39 ± 0.04[d]	144 ± 4[d]	147 ± 5[d]
0.052	19.23	1.038	0.630	0.41 ± 0.07[e]	305 ± 9[e]	316 ± 9[e]
0.034	29.41	1.059	0.835	0.73 ± 0.01[f]	360 ± 60[f]	380 ± 60[f]
1.95×10^{-2}	51.3	1.103	0.982	0.41 ± 0.06[e]	435 ± 100[e]	480 ± 111[e]
1.55×10^{-2}	64.5	1.129	0.775	0.37 ± 0.02[f]	580 ± 170[f]	650 ± 120[f]
1.41×10^{-2}	70.8	1.142	0.920	0.32 ± 0.08[f]	443 ± 75[f]	507 ± 87[f]
6.31×10^{-3}	159	1.317	0.775	0.38	634 ± 82[f]	835 ± 108[f]
5.01×10^{-3}	200	1.399	0.825	0.32 ± 0.04[d]	754 ± 271[d]	1054 ± 380[d]
4.79×10^{-3} [b]	209	1.418	0.937	0.42 ± 0.02[f]	500 ± 90[f]	700 ± 140[f]
3.72×10^{-3} [b]	269	1.538	0.825	0.44 ± 0.01[e]	630 ± 90[e]	970 ± 140[e]
2.00×10^{-3}	500	2.000	0.660	0.33 ± 0.02[e]	780 ± 120[e]	1570 ± 240[e]
2.24×10^{-4}	4460	9.96	0.710	0.32 ± 0.03[e]	516 ± 35[e]	5130 ± 340[e]

[a] Initial concentration of all Co(III) species. [b] $\mu = 1.0\ M$ ($NaClO_4$, $HClO_4$); for all other runs $\mu = 1.0\ M$ ($LiClO_4$, $HClO_4$). Note that k is a composite rate constant representing as it does the directly observed specific rate of disappearance of all cobalt(III) species present at a specific pH using the experimentally determined composite value of ϵ appropriate to that pH. [c] Mean and mean deviation of six determinations. [d] Mean and mean deviation of two determinations. [e] Mean and mean deviation of three determinations. [f] Mean and mean deviation of four determinations. [g] Mean and mean deviation of five determinations.

duction of a significant portion of the Co(III) complex by Cr^{2+}, both $[Co(III)]_0$ and A_0 had to be determined by extrapolation. Any errors in the calculated correction factors for $[Co(III)]_0$ and A_0 are reflected in the value of $[Co(III)]_\infty$.

The V^{2+} Reductions of *trans*-$CoL(OH_2)_2^{3+}$.—We have found the rates of reduction of the *trans*-diaquo complexes by V^{2+} to increase with pH. Our observations are summarized in Table VII.

Discussion

These *trans*-$CoL(OH_2)OH^{2+}$ complexes appear to have a very great tendency to polymerize. This polymerization has been a problem of concern to us since many of the electron-transfer reactions were run under conditions where polymer species apparently exist at significant levels at equilibrium. However, even under the most unfavorable conditions (the stopped-flow experiments in which $2 \times 10^{-4}\ M$ cobalt(III) solutions stood at high pH for up to 1 hr) the amount of dimer formed could not have exceeded 10% of the total cobalt. No absorbance changes were noted for the cobalt(III) reservoir solution during stopped-flow experiments, nor did any of the electron-transfer reactions exhibit kinetic peculiarities which could be attributed to the presence of more than one cobalt(III) species.

TABLE VII

KINETICS OF V^{2+} REDUCTIONS OF *trans*-$CoL(OH_2)_2^{3+}$ COMPLEXES[a]

$[H^+]$, *M*	$[Co(III)]_0$,[b] *M*	$10^5[V^{2+}]_0$, *M*	$10^{-2}k$,[c,d] M^{-1} sec^{-1}	$10^{-2}k$,[d,e] M^{-1} sec^{-1}
		L = *trans*[14]diene		
9.33×10^{-2}	0.947	0.400	2.1	2.2 ± 0.2
8.91×10^{-2}	0.937	0.238	3.5	3.7 ± 0.3
1.35×10^{-2}	1.900	0.814	2.8	2.9 ± 0.2
1.26×10^{-2}	2.040	0.392	8.8	9.6 ± 0.8
1.00×10^{-2}	1.900	1.610	4.5	4.4 ± 0.2
5.01×10^{-4}	1.884	0.907	19	20 ± 2
		L = teta		
0.112	1.02	0.585	14	14
0.100	0.845	0.258	24	26 ± 2
1.78×10^{-3}	1.02	0.326	160	145 ± 6
8.32×10^{-4}	2.04	0.683	176	165 ± 9
2.88×10^{-4}	2.04	0.569	278	380 ± 70

[a] μ = 1.0 *M* ($HClO_4$, $NaClO_4$); 25.0°. [b] Total initial concentration of Co(III) species. [c] Rate = $k'[CoL(OH_2)_2^{3+}][V^{2+}]$; second-order calculation. [d] Note that specific rate constants are calculated from the observed "composite" rate constants by correcting for the amount of $CoL(OH_2)OH^{2+}$ present. See footnote *b* of Table VI. [e] Average of second-order and pseudo-first-order calculations of *k*.

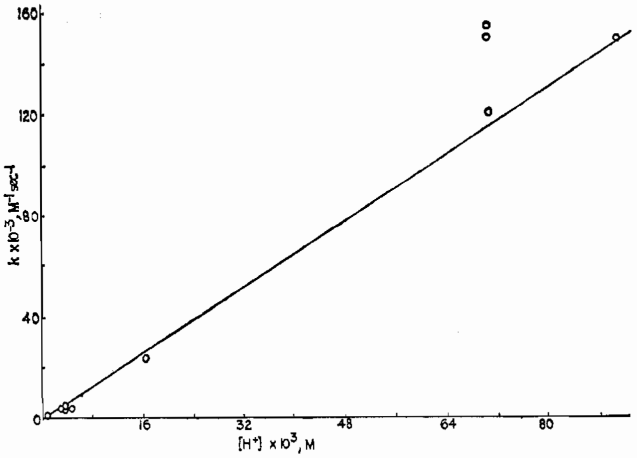

Figure 4.—Acid dependence of the apparent second-order rate constant for the $Ru(NH_3)_6^{2+}$ reductions of *trans*-Co(teta)(OH_2)OH^{2+}; μ = 0.10 *M* ($HClO_4$, $LiClO_4$); 25°. The line has a slope of 1.5×10^6 M^{-2} sec^{-1}.

TABLE VIII

APPARENT REACTIVITIES OF AQUO AND HYDROXY COMPLEXES OF COBALT(III) WITH VARIOUS REDUCING AGENTS

Oxidant	$k_{obsd}(Ru(NH_3)_6^{2+})$,[a] M^{-1} sec^{-1}	$[V^{2+}]$, *M*	$[Cr^{2+}]$, *M*	$E°$ (oxidant),[b] V
$Co(NH_3)_6^{3+}$	0.011[c]	3.5×10^{-3} [d]	0.8×10^{-4} [e]	0.1[f]
$Co(NH_3)_5OH_2^{3+}$	3.0[c]	0.5[d]	0.55[e]	0.33[g]
$Co(NH_3)_5OH^{2+}$	0.040[c]		1.5×10^6 [e,h]	
trans-$Co(en)_2(OH_2)_2^{3+}$			0.72[i]	
trans-$Co(en)_2(OH_2)OH^{2+}$			2.6×10^6 [h,i]	
trans-$Co(en)_2(NH_3)OH_2^{3+}$			0.44[i]	
trans-$Co(en)_2(NH_3)OH^{2+}$			0.22×10^6 [h,i]	
trans-Co(*trans*[14]diene)$(OH_2)_2^{3+}$	$(8 \pm 1) \times 10^2$ [j]	$(2.4 \pm 2) \times 10^2$ [j]	≤15[j]	0.565[j]
trans-Co(*trans*[14]diene)$(OH_2)OH^{2+}$	$(1.0 \pm 0.2) \times 10^2$ [j]	$(8.5 \pm 1) \times 10^2$ [j]	3.6×10^6 [h,j]	
trans-Co(teta)$(OH_2)_2^{3+}$	$(3.0 \pm 0.5) \times 10^3$ [j]	$(1.8 \pm 1) \times 10^3$ [j]	≤10^2 [j]	0.593[j]
trans-Co(teta)$(OH_2)OH^{2+}$	5×10^2 [j]	$(8.5 \pm 1) \times 10^3$ [j]	7×10^6 [h,j]	

[a] Apparent second-order rate constants for reactions indicated at 25° and ionic strength (μ) 1.0, except as indicated. [b] Reduction potentials. [c] Reference 15. μ = 0.20. [d] Reference 11b. μ = 0.40. [e] Reference 11b. [f] Reference 33. See discussion in ref 15. [g] Reference 41. [h] Assuming a simple bimolecular reaction between the hydroxy complex and Cr^{2+}, *i.e.*, using initial pH dependence of reaction rate. No inference about nonbridging ligand effects is possible; precursor complex formation is neglected. [i] R. C. Cannon and J. E. Earley, *J. Amer. Chem. Soc.*, **87**, 5264 (1965); **88**, 1872 (1966). [j] This work.

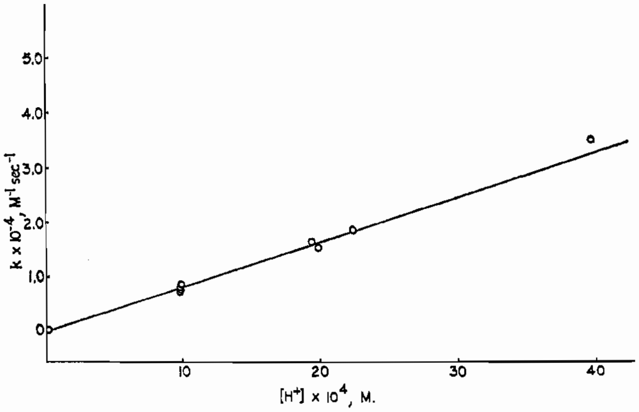

Figure 3.—Acid dependence of the apparent second-order rate constant for the $Ru(NH_3)_6^{2+}$ reduction of *trans*-Co(*trans*[14]diene)(OH_2)OH^{2+}; μ = 0.1 *M* ($HClO_4$, $LiClO_4$), 25°. The slope of the line is 8.2×10^6 M^{-2} sec^{-1}.

Outer-Sphere Reductions.—The $Ru(NH_3)_6^{2+}$ reductions of *trans*-Co(*trans*[14]diene) $(OH_2)_2^{3+}$ and *trans*-Co(teta)$(OH_2)_2^{3+}$ are very rapid; however this high reactivity seems to reflect the relatively good oxidizing ability of these cobalt complexes (Table VIII). In fact if we adopt the estimated value of 0.33 V for the reduction potential of the $Co(NH_3)_5OH_2^{3+,2+}$ couple,[44] then for the four reactions about which we have the appropriate information $RT \ln k \propto \Delta G°$ (see Figure 5). The constant of proportionality turns out to be 0.63 rather than the 0.5 predicted by Marcus.[45,46] However it appears that the *trans*-Co(*trans*[14]diene)$(OH_2)_2^{3+,2+}$ isotope exchange rate[47] seems to be about one order of magnitude faster than the $Co(NH_3)_6^{3+,2+}$ exchange rate[48] so the dependence of ln *k* on $\Delta G°$ may be very close indeed to that predicted by Marcus.

Similar trends in reactivity with $\Delta G°$ are exhibited by the V^{2+} and Cr^{2+} reactions. It has been noted previously[17] that free energy correlations of V^{2+} and Cr^{2+} reactions are often relatively crude. Some of the scatter must arise from mechanistic differences (*e.g.*, the Cr^{2+}–$Co(NH_3)_5OH_2^{3+}$ reaction proceeds by means of an inner-sphere mechanism while Cr^{2+}–$Co(NH_3)_6^{3+}$ is outer sphere[10,11]).

The *trans*-$CoL(OH_2)OH^{2+}$ complexes react more

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[44] R. G. Yalman, *Inorg. Chem.*, **1**, 16 (1962).

[45] (a) R. A. Marcus, *Discuss. Faraday Soc.*, **29**, 21 (1960); (b) *J. Phys. Chem.*, **67**, 853 (1963); (c) *Ann Rev. Phys. Chem.*, **15**, 155 (1964).

[46] See also the treatment of such linear free energy relations in ref 17. We are as usual neglecting the relatively insensitive correction factor, f_{12}, in the Marcus correlation.[17,45] Note that no correction has been made for differences in ionic strength.

[47] The specific rate of exchange has been found to be $\sim 10^{-7}$ M^{-1} sec^{-1} at 70°: N. A. P. Kane-Maguire, unpublished observations.

[48] Approximately 10^{-9} M^{-1} sec^{-1} at 64.5°: N. S. Biradar and D. R. Stranks, *Trans. Faraday Soc.*, **58**, 2421 (1963).

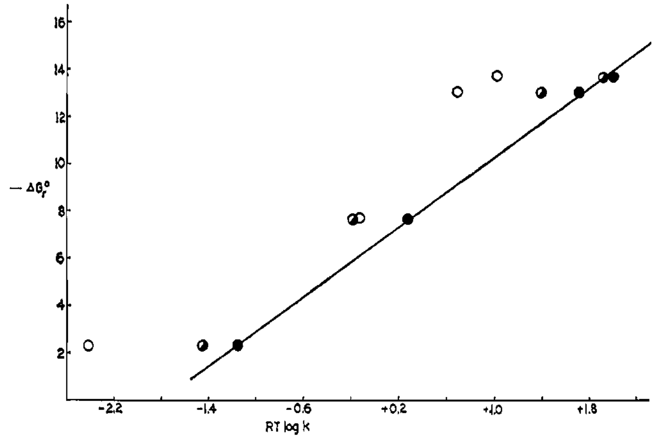

Figure 5.—Variations of rates of reduction of several cobalt(III) complexes with the reaction energetics ($\Delta G_r°$). $\Delta G_r°$ is the contribution to the total free energy of reaction due to the reversible cobalt(II)–cobalt(III) couples. In order of increasing contributions to the standard free energy of reaction, the couples are $Co(NH_3)_6^{2+,3+}$, $Co(NH_3)_5OH_2^{2+,3+}$, *trans*-Co(*trans*[14]diene)$(OH_2)_2^{2+,3+}$, and *trans*-Co(teta)$(OH_2)_2^{2+,3+}$. The line is drawn through data for the $Ru(NH_3)_6^{2+}$ reductions (solid circles). Data are also included for the Cr^{2+} reductions (open circles) and the V^{2+} reductions (half-open circles). Note that the entries for the Cr^{2+}–*trans*-$CoL(OH)_2)_2^{3+}$ reactions (L = teta and *trans*[14]diene) are upper limits.

slowly with $Ru(NH_3)_6^{2+}$ than do the corresponding *trans*-$CoL(OH_2)_2^{3+}$ complexes (Table VIII), in accord with our expectation for outer-sphere reactions. Presumably the V^{2+} reactions reported in this work are too fast to be accompanied by substitution into the first coordination sphere of V^{2+} [49–51] and should also be regarded as outer sphere. Therefore, we did not expect that V^{2+} would be more reactive with the *trans*-$CoL(OH_2)OH^{2+}$ complexes than the *trans*-$CoL(OH_2)_2^{3+}$ complexes (Table VIII) (although a very similar effect has been observed in the $Ru(NH_3)_5OH_2^{2+}$ reduction of $FeOH^{2+}$ and Fe^{3+} [52]). This inversion in reactivity of V^{2+} and $Ru(NH_3)_6^{2+}$ toward aquo and hydroxy complexes suggests that these "outer-sphere" reactions maybe bridged in the activated complex (*e.g.*, through hydrogen bonding when both reactants contain aquo ligands). The latter point has been made previously by other workers.[8,53] However, it should also be noted that in the present case we cannot unambiguously distinguish between the contributions of the reactions $V^{2+} + CoL(OH_2)OH^{2+}$ and $VOH^+ + CoL(OH_2)_2^{3+}$ to the enhanced reactivity at high pH (if the pK_a of V^{2+} is ≤ 9).[23]

The Cr^{2+} Reductions.—The basic features of the Cr^{2+} reduction of *trans*-Co(*trans*[14]diene)$(OH_2)_2^{3+}$ were described in a preliminary report of this work.[54] Table VI provides some additional documentation of the complex $[H^+]$ dependence of k_{obsd}. The data for the Cr^{2+} reduction of *trans*-CoL(teta)$(OH_2)_2^{3+}$ are qualitatively similar (Table VI). It is particularly important to note that the observed value of k^{55} at pH 6, where *trans*-Co(*trans*[14]diene)$(OH_2)OH^{2+}$ predominates, is only 8×10^5 M^{-1} sec^{-1} (Table VI), about 20% of the value predicted for the aquohydroxy complex on the basis of K_1 and the inverse acid dependence of k at high acidity. Similarly for the teta complex, k^{55} at pH 4 (where Co(teta)$(OH_2)OH^{2+}$ predominates) is only 5×10^5 M^{-1} sec^{-1}, less than 10% of the value predicted for the aquohydroxy complex. *These observations themselves indicate that any mechanistic analysis which attributes the pH dependence of Cr^{2+} reductions of the aquo complexes of cobalt(III) entirely to differing reactivities of the respective aquo and hydroxy complexes (e.g.,* reactions 7–9) *must be in error.* Other qualitative objections to such a model have been mentioned in the introduction to this paper.

$$CoL(OH_2)_2^{3+} \rightleftharpoons CoL(OH)_2OH^{2+} + H^+ \quad K_1 \tag{7}$$

$$CoL(OH_2)_2^{3+} + Cr^{2+} \longrightarrow CoL^{2+} + Cr^{3+} \quad k_8 \tag{8}$$

$$CoL(OH_2)OH^{2+} + Cr^{2+} \longrightarrow CoL^{2+} + CrOH^{2+} \quad k_9 \tag{9}$$

The complex dependence of these reactions on $[H^+]$ does imply a many-step mechanism with some (reversible or quasireversible) steps involving binuclear intermediates. The nearly first-order dependence on both [cobalt(III)] and $[Cr^{2+}]$ indicates that the intermediate species never predominate in concentration and cannot be formed from the reaction products under our experimental conditions. Such a complex dependence on $[H^+]$ and the limitations of the experimental determinations suggest that no particular rate law is likely to be truly unique.[56] A mechanistically useful type of function is of the type[54,57]

$$k_{obsd} = \frac{1 + a[H^+] + \ldots}{b + c[H^+] + d[H^+]^2 + \ldots} \tag{10}$$

where k_{obsd} is defined by

$$\frac{d[Co(III)]}{dt} = k_{obsd}\,[CoL(OH_2)_2^{3+}][Cr^{2+}]$$

The specific details of mechanisms involving binuclear intermediates are notoriously ambiguous.[58] Despite such ambiguities an additional point of considerable significance can be made about the present system.

If we assume that OH^- affects the cobalt(III)–cobalt(II) and chromium(III)–chromium(II) couples similarly, then we may estimate the "equilibrium" constants for the charge redistribution reactions

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(49) B. Baker, M. Orhanovic, and N. Sutin, *J. Amer. Chem. Soc.*, **89**, 722 (1967).

(50) M. V. Olson, T. Kanizawa, and H. Taube, *J. Chem. Phys.*, **51**, 289 (1969).

(51) N. Sutin, *Accounts Chem. Res.*, **1**, 225 (1968).

(52) T. J. Meyer and H. Taube, *Inorg. Chem.*, **7**, 2369 (1968).

(53) J. Halpern, *Quart. Rev., Chem. Soc.*, **15**, 207 (1961).

(54) M. P. Liteplo and J. F. Endicott, *J. Amer. Chem. Soc.*, **91**, 3982 (1969).

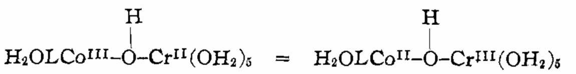
(55) This is k as defined by $d[Co(III)]/dt = k[Co(III)][Cr^{2+}]$ when [Co(III)] is the total cobalt(III) concentration.

(56) For example in addition to algebraic fractions of the type in eq 10, the kinetic data may be fitted by exponential functions of $[H^+]$ or by algebraic functions of $[H^+]^{1/2}$. We have chosen (arbitrarily) to use functions of the type in eq 10 to illustrate the mechanistic principles *required* by our observations since it is easier to fit simple, intuitively appealing mechanistic models to such algebraic functions.

(57) In a preliminary report[54] of this work we pointed out that our kinetic data could in principle be fitted by a very simple form of (10) in which higher order terms are neglected and $b = 0$. As brought to our attention by a referee, such a simple algebraic function of $[H^+]$ is not compatible with the simple mechanistic model which we had chosen (arbitrarily) to *illustrate* the mechanistic principles required by our observations. We have attempted to make clear that the type of information gathered in the present study cannot determine a *unique* rate expression and that any given rate expression of the required complexity is consistent with several mechanistic models (see ref 58). The importance of the present study lies in the requirements which our observations must impose on any mechanistic model. In order to minimize the possibility of confusing the algebraic analysis of some specific model with the important mechanistic points discussed in the text above (a matter in which we appear to have confused the referee), we have relegated to the Appendix the detailed algebraic analysis of two simple mechanistic models. We wish to emphasize that no particular "truth content" can be ascribed to these models beyond their illustration of those points raised in the text above.

(58) A. Haim, *Inorg. Chem.*, **5**, 2081 (1966).

(eq 11) as 2 × 10^{16} and 8 × 10^{16} when L is *trans*[14]diene and teta, respectively. Since even for an allowed electronic transition k_{11} (the forward rate constant) would be less than 10^{13} sec^{-1}, in order for the chemical behavior of successor complexes (*i.e.*, of the type $H_2OLCo^{II}–OH–Cr^{III}(OH_2)_5$) to affect the observed kinetics, the lifetimes of such successor complexes would have to exceed 10^3 sec. This is clearly not the case. Thus the complex acid dependence (eq 10) of the Cr^{2+} reductions is to be attributed to the formation and chemical behavior of precursor complexes. Recently, Cannon and Gardiner[59] reported that the reduction of the nitrilotriacetic acid complex of pentaamminecobalt(III) by iron(II) involves the formation of a precursor complex whose lifetime they determined to be 10 sec. Evidence for precursor complexes has also been found by Patel, Ball, Endicott, and Hughes[39] in $Co(en)_2ACl^{2+}$–Cr^{2+} reactions and by Liang and Gould[60] in salicylatopentaamminecobalt(III)–Cr^{2+} reactions.



$$H_2OLCo^{III}–\overset{\overset{H}{|}}{O}–Cr^{II}(OH_2)_5 = H_2OLCo^{II}–\overset{\overset{H}{|}}{O}–Cr^{III}(OH_2)_5 \quad (11)$$

Specific mechanistic models which illustrate the above points might combine reactions 7 and 12 and/or reaction 13 with reactions 14 and 15 (k_{OH} or k_O for X = OH^- or O^{2-}, respectively). Two of the possible models are considered in the Appendix. It is important to note that there is nothing in the above combinations of hypothetical reactions which requires that any individual step have rates in excess of diffusion-controlled limits or that the reactants be depleted in the formation of precursor complexes. It is also to be recalled that a step such as (12) or (13) is required by our experimental observations as discussed in the preceding paragraphs.

$$CoL(OH_2)OH^{8+} + Cr(OH_2)_6^{2+} \rightleftharpoons (H_2O)LCo^{III}–OH–Cr^{II}(OH_2)_5 + H_2O \quad (12)$$

$$CoL(OH_2)_2^{3+} + Cr(OH_2)_6^{2+} \rightleftharpoons (H_2O)LCo^{III}–OH–Cr^{II}(OH_2)_5 + H^+ + H_2O \quad (13)$$

$$(H_2O)LCo^{III}–OH–Cr^{II}(OH_2)_5 \rightleftharpoons (H_2O)LCo^{III}–O–Cr^{II}(OH_2)_5 + H^+ \quad (14)$$

$$(H_2O)LCo^{III}–X–Co^{II}(OH_2)_5 \longrightarrow \text{products} \quad (15)$$

Summary Statement

We have used two macrocyclic complexes of cobalt(III) as electron-transfer oxidants in order to examine some ideas concerning reactivity differences which accompany changes in bridging and/or nonbridging ligands.

The changes in nonbridging ligands in the present study are about as simple as seems presently possible: in one case (the teta complex) all four coordinated nitrogen atoms are secondary amines, while the other complex (*i.e.*, *trans*[14]diene) contains two secondary amine nitrogen atoms and two imine nitrogen atoms coordinated to cobalt(III). In both cases the superficial structural features of the complexes are similar. As in previous studies[17,39,61] we find that a change in the kind of nonbridging ligand (*i.e.*, in the present case whether amine or imine) coordinated to cobalt(III) results in a change of reactivity. However, in the present case these reactivity changes clearly parallel changes in the free energy of reaction. The present study thus lends additional substance to a previous argument[17] that free energy changes tend to dominate the reactivity patterns of cobalt(III) complexes. Further studies of electron-transfer reactions involving reversible cobalt(III)–cobalt(III) couples would be of obvious interest.

The Cr^{2+} reductions of these $CoL(OH_2)_2^{3+}$ complexes presumably proceed through the usual bridged activated complex. However, in the present study we have been able to demonstrate that $CoL(OH_2)OH^{2+}$ is about an order of magnitude less reactive than implied by the acid-dependent reactivity of $CoL(OH_2)_2^{3+}$. The complex acid dependence of the rate law and the thermodynamics of the net oxidation reduction reactions implicate precursor complexes in the kinetically significant steps. It is proposed therefore that the extraordinary enhancement of rate which is observed in many electron-transfer reactions when OH^- serves as the bridging ligand in the activated complex is at least partly a result of the relative stability of hydroxy-bridged binuclear complexes. It is not necessary to postulate that the OH^- ligand has any kind of unique capacity to "conduct" electrons from one metal to another.

Appendix. Analysis of Mechanistic Models Involving Precursor Complexes

It is useful to demonstrate that at least some physically sensible mechanistic models are consistent with the "empirical rate law" (eq 10). Although there is little point in searching for all the models consistent with (10) (*e.g.*, see ref 58), consideration of one or two of the simpler mechanisms does help focus thinking about the issues raised in the text. We present these two mechanisms only to illustrate the chemical issues raised in the text and wish to make no claim that either is the "correct" mechanism. Both mechanisms I and II seem reasonably consistent with our data in the pH range 0–3 (this limitation is imposed because our data at higher pH's are limited and because consideration of some of these data would force us to introduce additional protolytic equilibria allowing for the ionization of some of the nonbridging water molecules in the precursor complexes). We find that mechanism I is a bit harder to fit to the data for pH >2, but the discrepancies seem to average around 40% in this region and we would not want to exclude the mechanism on this basis alone. Mechanism II is a little more easily fitted to the experimental data. A linear combination of mechanisms I and II would fit even better.

Mechanism I.—Consider reactions 13–15 as proposed in our preliminary communication.[54] If one assumes a steady state in the concentration of intermediates, then

$$k_{obsd} = \frac{k_{13}k_{OH} + \dfrac{k_{13}k_Ok_{14}}{k_{-14}[H^+] + k_O}}{k_{-13}[H^+] + k_{14} + k_{OH} - \dfrac{k_{-14}k_{14}[H^+]}{k_{-14}[H^+] + k_O}}$$

This expression may then be rearranged (as pointed out by a referee) to obtain (16) which is an algebraic form consistent with (10). As noted (16) is rather difficult to

$$k_{obsd} = \frac{k_{13} + k_{13}\dfrac{k_{OH}}{k_OK_{14}}[H^+]}{1 + \dfrac{k_{OH}}{k_OK_{14}}[H^+] + \dfrac{k_{-13}}{k_OK_{14}}[H^+]^2} \quad (16)$$

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(59) R. D. Cannon and J. Gardiner, *J. Amer. Chem. Soc.*, **92**, 3800 (1970).

(60) A. Liang and E. S. Gould, *ibid.*, **92**, 6791 (1970).

(61) (a) C. Bigano and R. G. Linck, *Inorg. Chem.*, **7**, 908 (1968); (b) P. R. Guenther and R. G. Linck, *J. Amer. Chem. Soc.*, **91**, 3769 (1969); (c) R. G. Linck, *Inorg. Chem.*, **9**, 2529 (1970).

fit to the experimental data, but approximate fits are provided with $k_{13} \approx 3 \times 10^5\ M^{-1}\ \text{sec}^{-1}$, $k_{-13}/k_{\text{O}}K_{14} \approx 10^5\ M^{-2}$, and $k_{\text{OH}}/k_{\text{O}}K_{14} \approx 10^3\ M^{-1}$ for the Co(*trans*-[14]diene)$(\text{OH}_2)_2{}^{3+}$–Cr^{2+} reaction, and $k_{13} \approx 5 \times 10^6\ M^{-1}\ \text{sec}^{-1}$, $k_{-13}/k_{\text{O}}K_{14} \approx 10^6\ M^{-2}$, and $k_{\text{OH}}/k_{\text{O}}K_{14} \approx 3 \times 10^3\ M^{-1}$ for the Co(tet*a*)$(\text{OH}_2)_2{}^{3+}$–Cr^{2+} reaction. Thus physically possible rate parameters can be assigned (note that "estimates" are not possible) for this mechanism so that K_{13} is $\sim 10^{-4}$ for the former and $\sim 10^{-3}$ for the latter reaction. Therefore the maximum amount of reactants in the form of precursor complexes need be not more than 1 or 10%, respectively, even at pH 4.

Mechanism II.—Consider reactions 7, 12, 14, and 15. The appropriate steady-state approximations and some algebraic manipulation lead to

$$k_{\text{obsd}} = \frac{K_1}{[\text{H}^+]}\left\{\frac{1 + a[\text{H}^+]}{b + c[\text{H}^+]}\right\} \qquad (17)$$

where

$$a = \frac{k_{\text{OH}}k_{-14}}{(k_{\text{OH}} + k_{14})k_{\text{O}}}$$

$$b = \frac{(k_{-12} + k_{\text{OH}})}{k_{12}k_{\text{O}}(k_{\text{OH}} + k_{14})}$$

$$c = \frac{k_{-12} + k_{\text{OH}} + k_{14}}{k_{12}(k_{\text{OH}} + k_{14})}$$

Equation 17 is also consistent with (10). Using values of K_1 from Table I we find $a/c = 3.6 \times 10^6\ M^{-1}\ \text{sec}^{-1}$ and $b = 8 \times 10^{-7}\ M^{-1}\ \text{sec}^{-1}$ for the Co(*trans*[14]diene)$(\text{OH}_2)_2{}^{3+}$–Cr^{2+} reactions and $a/c = 0.65 \times 10^7\ M^{-1}\ \text{sec}^{-1}$ and $b = 1.2 \times 10^{-6}\ M^{-1}\ \text{sec}^{-1}$ for the Co(tet*a*)$(\text{OH}_2)_2{}^{3+}$–Cr^{2+} reaction. For this mechanism assignment of possible rate parameters (again "estimates" are not possible) can result in $K_{12} \approx 10^{-2}\ M^{-1}$ for both reactions. Thus under our reaction conditions (*i.e.*, [reactants] $\leq 10^{-4}\ M$) this mechanism does not require more than 1% of the reactants be in the form of precursor complexes even at a pH of 4.

As noted above these two mechanisms are only marginally distinguishable by our experimental data with mechanism II being slightly preferred. Either mechanism is adequate to illustrate the significant features of our study. Other mechanisms can be proposed. However our work indicates that any proposed mechanism must involve precursor complex formation and some acid–base chemistry of the precursor intermediates.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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Phenylacetyl–Benzyl(carbonyl) Rearrangement at Iridium. A Kinetic Study

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The oxidative additions of variously substituted phenylacetyl chlorides to *trans*-chlorobis(triphenylphosphine)dinitrogeniridium(I) give five-coordinated phenylacetyliridium complexes, **1**. These complexes rearrange in solution to six-coordinated benzyl(carbonyl) complexes, **2**. The kinetics of this rearrangement have been investigated and mechanistic implications of the kinetic data are discussed.

Insertion or ligand migration processes are important in reactions which are homogeneously catalyzed by complexes of transition metals.[2] Information presently available on migration reactions is predominantly comprised of stereochemical and kinetic studies of the methyl- or acetylpentacarbonylmanganese and related systems.[2,3] Considerable attention has been directed to determine whether these reactions proceed by CO insertion or methyl migration, but information on the actual migration step has been elusive. Since the rate-determining step in the conversion of acetylmanganese complexes to methyl(carbonyl)manganese complexes involves the loss of CO or another ligand and not the migration of the methyl moiety to manganese,[2] intimate details of the actual migration step have not been obtained from studies of the decarbonylation of acetylmanganese complexes. The rate-determining step in the decarbonylation of $\text{CH}_3\text{COMn(CO)}_5$ and in the carbonylation of $\text{CH}_3\text{Mn(CO)}_5$ is presumably the formation of five-coordinated intermediates of manganese (d^6 electronic configuration).[2] Such intermediates have not been detected or isolated for the manganese system. Herein, we report isolation of five-coordinated phenylacetyliridium(III) complexes (d^6 electronic configuration) and kinetic studies of the rearrangement of these five-coordinated complexes to six-coordinated benzyl(carbonyl)iridium(III) complexes. Five-coordinated acyl complexes have been recently proposed[4] as intermediates in the decarbonylation of complexes such as $\text{Ir(CO)}_2\text{Cl}_2(\text{CH}_3)\text{As}(\text{C}_6\text{H}_5)_3$.

Results and Discussion

The addition of various substituted phenylacetyl chlorides to suspensions of *trans*-chlorobis(triphenylphosphine)dinitrogeniridium(I)[5] in benzene results in evolution of nitrogen and formation of red solutions from which fibrous orange crystals of the five-coordinated acyl complexes **1** are precipitated. These five-coordinated complexes which have been isolated and

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